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PROCESS FOR RESISTING CORROSION BY ALIPHATIC ACIDS

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The present invention relates to the treatment of organic acid mixtures containing formic acid, more particularly those obtained by the oxidation of organic compounds.

In operations involving the treatment of organic acids, such as distillation operations, it is necessary to use corrosion resistant materials of construction because of the highly corrosive nature of mixtures containing formic acid, acetic acid and other aliphatic acids; in particular formic acid is highly corrosive. As a result stainless steel is a usual material for the construction of apparatus to be used for such operations. Stainless steel, however, is corroded by formic acid, and investigations have been made to determine the conditions under which this corrosion will be a minimum. These investigations have shown (Lane, Golden and Acheman, Industrial & Engineering Chemistry, 1953, volume 45, page 1067), that the corrosion of stainless steel by hot formic acid is a maximum in the presence of air and a minimum in the absence of air, and these findings have been verified by the applicants.

It is an object of the present invention to provide a process involving the heat treatment of aliphatic acids obtained by the oxidation of hydrocarbons or ketones, containing formic, acetic and other acids, in apparatus constructed at least in part of stainless steel, in which the corrosion of stainless steel is reduced to a minimum.

Accordingly the present invention is for a process involving the heat treatment in apparatus constructed at least in part of stainless steel, of a mixture of aliphatic acids including a minor proportion of formic acid obtained by the oxidation with molecular oxygen of hydrocarbons or ketones which comprises passing an oxygen containing gas through the mixture during the heat treatment.

The heat treatment involved is most usually a distillation operation. The process of the invention however is not restricted to distillations, but may equally be applied to other operations involving the heat treatment of mixtures of aliphatic acids.

The mixture of aqueous aliphatic acids containing a minor proportion of formic acid generally comprises an aqueous mixture of formic, acetic, propionic and butyric acids wherein the formic acid content is less than about 25% by weight of the mixture. Such acid mixtures are obtained for example by the processes described in copending U.S. applications Ser. Nos. 385,272; 385,182 and 385,306 which relate to the production of aliphatic acid by the oxidation of lower paraffinic hydrocarbons. In such oxidations, ketones such as acetone and methyl ethyl ketone are intermediate products and accordingly ketones may serve as starting materials in the oxidation reaction to produce the mixture of aliphatic acids to be treated

according to the invention. The oxidation product is usually submitted to a series of distillation steps to recover the acids, and the invention is useful with any of the acid containing mixtures so obtained, as well as with the oxidation product itself. Even during the distillation of formic acid from higher acids, the invention may be used to reduce corrosion in at least the base of the still and the lower parts of the column.

The stainless steel employed in the construction of the apparatus used in the process of the invention may be any of the stainless steels which are available. Such steels are the nickel-chromium steels for example Firth-Vickers FMB containing 18% chromium, 8.5% nickel, 2.75% molybdenum and FDP containing 18% chromium, 8.5% nickel, 0.6% titanium and like steels.

The oxygen containing gas may comprise oxygen, air, ozone or the like. It is generally most convenient and economical to employ air as the oxygen containing gas. The oxygen containing gas is most conveniently passed through the mixture by passing a stream of the gas in at the base of the apparatus and withdrawing the gas at some point at the top of the apparatus.

The following examples are given to illustrate the process of the present invention.

Example 1

Two strips of stainless steel containing 18% chromium, 8% nickel were partially immersed in a mixture of wet acids, obtained by the oxidation of paraffin hydrocarbons of 4–8 carbon atoms, and removal of light and heavy ends, of the composition:

	Percent by weight
Water	28
Formic acid	11
Acetic acid	54
Propionic acid	5
Butyric acid	1
Neutrals	1

at the boiling point (100–105°), in two separate vessels; through one vessel a very slow stream of air was passed, through the other a very slow stream of nitrogen. The corrosions produced were as follows:

	Corrosion Penetration (inches×10⁻³/year)	
	Period 1 (7 days)	Period 2 (7 days)
Nitrogen cover	93.2	68.4
Air cover	0.09	0.00

Example 2

A strip of stainless steel containing 18% chromium, 8.5% nickel, 0.6% titanium was partially immersed in wet acids, obtained by the oxidation of paraffin hydrocarbons, of the composition:

	Percent by weight
Water	28
Formic acid	11
C_2 to C_4 acids	60
Neutrals	1

at the boiling point (100–105°), while a very slow stream of ozonized oxygen was passed in. The corrosion produced, over a period of 7 days, corresponded to a penetration rate of 0.0001 inch/year.

Example 3

The corrosions produced on two samples of stainless

steel were determined by a dynamic method. The strips were whirled, at a peripheral speed of 7.1 feet/second, through boiling wet acids, obtained by the oxidation of paraffin hydrocarbons, of the composition:

	Percent by weight
Water	28
Formic acid	11
C_2 to C_4 acids	60
Neutrals	1

a slow stream of air was injected initially, and was subsequently changed to one of nitrogen. The great increase in corrosion brought about in the absence of air is shown in the following table:

Grade of stainless steel	Strip No.	Corrosion Penetration (inches×10⁻³/year) Period 1	Period 2	Period 3
Firth Vickers FMB	A	0.4 (air)	0.0 (air)	8.7(N_2)
	B	1.1 (air)	0.0 (air)	8.0(N_2)
Firth Vickers FDP	A	0.0 (air)	0.5 (air)	30.4(N_2)
	B	0.0 (air)	0.0 (air)	29.6(N_2)

Example 4

Stainless steel corrosion strips were placed in the kettle of a glass continuous still employed for topping a paraffinic hydrocarbon oxidate of composition:

	Percent by weight
Water	20
Formic acid	4.5
C_2 to C_4 acids	25.5
Neutrals	45
Higher acids and highers	5

In the first two periods of operation a slow stream of nitrogen was blown into the kettle of the still, and taken off at the stillhead; in the last two periods a slow stream of air was substituted for the nitrogen. The advantageous effects produced by the presence of air are shown in the following table:

Grade of stainless steel	Position of strip	Corrosion Penetration (inches×10⁻³/year) Period 1	Period 2	Period 3	Period 4
Firth Vickers FDP	partly immersed.	66.3 (N_2)	76.8 (N_2)	0.0 (air)	0.0 (air)
Firth Vickers FMB	totally immersed.	6.7 (N_2)	54.4 (N_2)	0.0 (air)	0.0 (air)

Example 5

Stainless steel corrosion strips were placed in the kettle, at the feed point and in the stillhead of a glass continuous still employed for topping a wet acid mixture, obtained by the oxidation of paraffin hydrocarbons of the composition:

	Percent by weight
Water	28
Formic acid	11
C_2 to C_4 acids	60
Neutrals	1

A slow stream of air was blown into the kettle of the still and taken off at the stillhead. The corrosions measured are shown in the following table:

Grade of stainless steel	Position of strip	Corrosion Penetration (inches×10⁻³/year) Period 1 (2 days)	Period 2 (2 days)
Firth Vickers FDP	feedpoint	0.0	5.4
	kettle-totally submerged	0.12	0.0
	kettle-partly submerged	0.0	0.0
Firth Vickers FMB	kettle-totally submerged	0.0	0.0
	kettle-partly submerged	0.0	0.0

Example 6

Stainless steel corrosion strips were immersed in the stated liquids at the boiling point for periods each of 1 week duration. The wet acids were obtained by the oxidation of a paraffinic fraction of boiling range 15°–95° C., and had approximately the same composition as the wet acids employed in Example 3.

Corroding Liquid	Cover	Corrosion Penetration (inches×10⁻³)/year) Period 1	Period 2	Period 3
Wet Acids	air	0.1	nil	nil
	nitrogen	15.0	9.1	4.3
Formic Acid (Analytical Reagent Grade 98–100%)	air	14.7	9.4	19.2
	nitrogen	3.4	9.0	8.9
Aqueous Formic Acid (Analytical Reagent Grade 73% by weight+water 27% by weight).	air	25.9	27.2	-------
	nitrogen	5.8	7.4	-------

We claim:

1. A process involving the heat treatment in apparatus constructed in major part of stainless steel, of a mixture of aliphatic acids obtained by the oxidation with molecular oxygen of a substance selected from the group consisting of hydrocarbons and ketones, which comprises passing molecular oxygen through the mixture containing not more than 25% formic acid while in contact with said stainless steel during the heat treatment to inhibit corrosion of said stainless steel.

2. A process involving the heat treatment in apparatus constructed in major part of stainless steel, of a mixture of aliphatic acids whose carbon chains have not over 4 carbon atoms, obtained by the oxidation with molecular oxygen of a substance selected from the group consisting of hydrocarbons and ketones, which comprises passing molecular oxygen through the mixture containing not over 11% formic acid while in contact with said stainless steel during the heat treatment to inhibit corrosion of said stainless steel.

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